Soil dissipation and biological activity of metolachlor and *S*-metolachlor in five soils

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Abstract: The resolved isomer of metolachlor, *S*-metolachlor, was registered in 1997. New formulations based primarily on the *S*-metolachlor isomer are more active on a gram for gram metolachlor basis than formulations based on a racemic mixture of metolachlor containing a 50:50 ratio of the *R* and *S* isomers. The labelled use rates of *S*-metolachlor-based products were reduced by 35% to give equivalent weed control to metolachlor. However, several companies have recently registered new metolachlor formulations with the same recommended use rates for weed control as *S*-metolachlor. This research was done to compare the soil behaviour and the biological activity of metolachlor and *S*-metolachlor in different soils under greenhouse and field conditions. Although K_d ranged from 1.6 to 6.9 across the five soils, there were no differences in the binding of metolachlor and *S*-metolachlor to soil or in the rate of soil solution dissipation in a given soil. However, both greenhouse and field studies showed that *S*-metolachlor was 1.4–3-fold more active than metolachlor against *Echinochloa crus-galli* (L.) Beauv. in five different soils and that *S*-metolachlor was more active than metolachlor in three Colorado field locations. When the rates of metolachlor and *S*-metolachlor were adjusted for *S* isomer concentrations in the formulations, there were no differences between the formulations in field, greenhouse or bioassay studies. Thus herbicidal activity is due to the *S* isomers, with the *R* isomers being largely inactive.

Keywords: acetanilide herbicide; racemic mixture; soil binding; soil dissipation; metolachlor; *S*-metolachlor

1 INTRODUCTION

Metolachlor was commercialised in 1977, providing control of grasses and small-seeded broadleaves in corn (*Zea mays* L.), soybean (*Glycine max* (L.) Merr.) and many other crops.[1] In 1998, approximately 32% of the corn and 4% of the soybean hectareage in the USA were treated with metolachlor at an average rate of 2.1 kg ha^{-1}.[2]

Metolachlor is composed of four isomers, an *R* isomer pair and an *S* isomer pair (Fig. 1). In 1982, Moser *et al*.[3] reported on the synthesis and separation of the resolved isomers of metolachlor, showing that the *S* isomers had at least 20-fold greater pre-emergence activity on seven grasses and three broadleaf weeds than the *R* isomers. These results suggest that 95% of the herbicidal activity of metolachlor is due to the *S* isomers. Similarly, dimethenamid, an *N*-thienyl chloroacetamide, is composed of *R* and *S* isomers, and the *S* isomers were found to be 30-fold more active than the *R* isomers on 13 weeds.[4] Many herbicides, such as the ACCase inhibitors, show similar differences between racemic mixtures and resolved isomers, and these herbicides are now sold as the resolved isomers.[1]

S-Metolachlor is approximately 88% *S* isomer and 12% *R* isomer.[3] This enrichment of the *S* isomer is accomplished through a selective synthetic manufacturing process.[3] *S*-Metolachlor is 1.4–1.6-fold more active than the metolachlor formulation on a gram for gram basis.[5,6] *S*-Metolachlor was commercialised in 1997 and rapidly displaced metolachlor in Syngenta's product line. The incentive for this displacement was the reduction in total herbicide load applied to the environment together with the concomitant reduction in user handling of the chemical.[7] Recommended use rates of *S*-metolachlor were 35% less than those of metolachlor.[8] In 1998 the average rate of metolachlor applied to corn was 2.1 kg ha^{-1}, whereas in 2003 the average rate of *S*-metolachlor applied to corn was 1.5 kg ha^{-1}.[2]

Recently, several generic metolachlor products (e.g. Stalwart™, Sipcam Agro USA, Inc., Roswell, GA, USA) have been commercialised with the same recommended use rates as *S*-metolachlor products for controlling the same weed species.[8]

Little research has been conducted comparing metolachlor with *S*-metolachlor applied at the same rates. Although it has been reported that most of the herbicidal activity of metolachlor is due to the *S* isomers, do the *R* isomers contribute to the total herbicidal activity of the racemic mixture? Are there any differences in the availability of these two forms of

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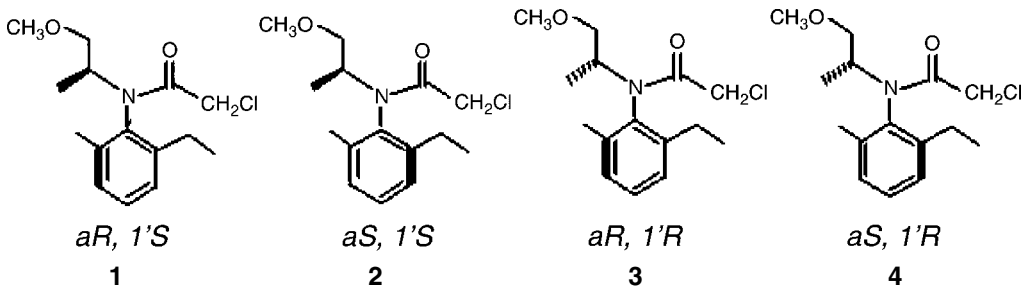

Figure 1. Structures of different racemic forms of metolachlor.

metolachlor in the soil or in their rates of dissipation? Will the level of efficacy of the two products be the same if they are applied at the same rate based on weight? The objective of this research was to compare the herbicidal activity of *S*-metolachlor with that of metolachlor and to determine the effect of soil type on the binding and availability of *S*-metolachlor compared with metolachlor.

2 MATERIALS AND METHODS

2.1 Chemicals

Formulated and technical metolachlor and *S*-metolachlor were supplied by Syngenta Crop Protection (Greensboro, NC, USA). The ratios of *S* isomers to *R* isomers in the two formulations were: metolachlor, 50:50; *S*-metolachlor, 88:12. The analytical standard was 98.5% pure.

2.2 Soils

Approximately 25 kg quantities of different soils were collected from various locations throughout the USA. The characteristics of these soils are shown in Table 1. Water-holding capacity was determined via pressure plate analysis,[9] and soil textures and properties were analysed by MDS Harris Laboratory (MDS Harris Agronomic Services, Lincoln, NE, USA). All soils were air dried and sieved to pass a 2 mm mesh prior to use. Soils were stored at 25 °C after drying.

2.3 Batch slurry equilibration

Herbicide binding was determined by the batch slurry equilibration technique.[10] Each assay consisted of four replications and was repeated three times. Air-dried soil (10 g) was placed in a 50 ml centrifuge tube with a Teflon-lined cap, and 10 ml of a solution containing 0.02 M calcium chloride, 0.5 mM mercuric chloride and 1 $\mu g\,ml^{-1}$ of either metolachlor or *S*-metolachlor was added. The tube was shaken for 24 h. Preliminary studies showed that equilibrium was reached during this period. The sample was removed from the shaker and centrifuged for 20 min at 2000 × *g*. A 3 ml aliquot of the equilibrium solution supernatant was transferred to a 10 ml test tube with a Teflon-lined cap, and 3 ml of water-saturated toluene was added. The tube was shaken for 1 h and then centrifuged for 5 min at 1000 × *g* to separate the layers. The toluene phase was transferred to a 2 ml volumetric flask to which 10 µl of a 0.1 $mg\,ml^{-1}$ metribuzin internal standard solution was added.

Herbicide concentrations in the toluene phase were analysed using a gas chromatograph equipped with a mass spectrometer (Hewlett Packard HP-5890 gas chromatograph, HP-5972 mass quadrupole, Agilent Technologies, Palo Alto, CA, USA), by monitoring the masses for metribuzin (*m*/*z* 198, 199, 214) and metolachlor (*m*/*z* 162, 238). An HP 5MS 30 mm × 0.25 mm column was used with a flow of helium at 1.5 ml min^{-1}. The injection temperature was 250 °C and the detector temperature was 280 °C. The programme for detecting metolachlor was as follows: initial oven temperature 80 °C (hold 1 min), ramped at 20 °C min^{-1} to 230 °C, then held at 230 °C for 2.5 min, with a run time of 11 min. Under these conditions the retention times of metribuzin and metolachlor were 8.78 and 9.45 min respectively. The detection limit was 0.1 $\mu g\,ml^{-1}$ for each herbicide. Quality control samples consisting of water spiked with herbicide at 1 and 0.25 $\mu g\,ml^{-1}$ were included in every run and showed >99% recovery of the herbicides by toluene from water. This procedure did not differentiate between metolachlor and *S*-metolachlor.

The amount of herbicide adsorbed by the soil was determined by the difference between the initial concentration of herbicide in the soil solution and the

Table 1. Soil properties for greenhouse and dissipation studies

Name	Location	Soil series	pH	OM (%)	CEC (meq 100 g^{-1})	Water-holding capacity[a] (%)
Gilcrest	Gilcrest, CO	Julesburg sandy loam	7.4	1.5	8.4	7.2
Minnesota	Redwood Falls, MN	Webster clay loam	7.1	5.6	38.7	31
Nebraska	York, NE	Hastings clay loam	6.7	3.5	20.6	22.8
San Luis Valley	Center, CO	Norte Gravelly sandy loam	7.4	1.7	12.5	11.2
Wisconsin	Arlington, WI	Plano clay loam	6.7	3.3	22.5	22

[a] −33 kPa water tension.

Pest Manag Sci **62**:617–623 (2006)
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final concentration after equilibration with the soil. The adsorption coefficient (K_d) was calculated as

$$K_d = \frac{(\text{herbicide sorbed to soil } (\mu g\, g^{-1}))}{(\text{herbicide in solution } (\mu g\, ml^{-1}))} \quad (1)$$

2.4 Dissipation of herbicide in soil solution

The change in concentration of metolachlor and *S*-metolachlor in the soil solution over time was determined using a centrifugal double-tube method.[11,12] Each assay consisted of four replications and was repeated. Air-dried soil (100 g) was placed in a 250 ml jar with a Teflon-lined lid and treated with enough water to reach 105% of field capacity (−33 kPa). The water contained either metolachlor or *S*-metolachlor at a level to reach a final concentration of 10 mg kg^{-1} dry soil. The jar was shaken to achieve complete mixing and then incubated at 25 °C. The weight of the jar was monitored and there was minimal water loss over time. At various intervals, 15 g of soil was removed from the jar and placed in a 50 ml centrifuge tube that contained an insert fitted with a 0.45 μm PVDF filter (Whatman VectaSpin® 20, VWR/Sargent Welch Scientific Co., Buffalo Grove, IL, USA). The soil and tube were centrifuged for 60 min at 2000 × *g*. The filtrate (soil solution) was transferred to a 15 ml test tube equipped with a Teflon-lined cap and the volume of soil solution water was measured by weight. Water-saturated toluene (2 ml) was added to the tube and shaken for 60 min. A metribuzin internal standard (10 μl, 0.2 mg ml^{-1}) was added and the tube was centrifuged for 10 min at 500 × *g*. A 1 ml aliquot of the toluene layer was transferred to a sample vial and the concentration of metolachlor or *S*-metolachlor was measured as described in Section 2.3.

2.5 Microtitre plate bioassay

A bioassay was conducted to compare the herbicidal activity of metolachlor and *S*-metolachlor in agar. A solution containing 2 μg ml^{-1} of either metolachlor or *S*-metolachlor was prepared by diluting a 1 mg ml^{-1} stock solution in acetonitrile with 50% Murashige and Skoog (M&S) basal salts solution (Sigma Aldrich Corporation, St Louis, MO, USA). This solution was serially diluted seven times by adding 6 ml of the herbicide solution to 2 ml of 50% M&S solution, resulting in concentrations ranging from 2 to 0.84 mg litre^{-1}. A 125 μl aliquot of each solution was pipetted into a well of a 96-well microtitre plate (VWR/Sargent Welch Scientific Co.). Agar (0.7 g) was dissolved in water (100 ml) by heating, cooled to <60 °C, and 125 μl of this solution was added to each well of the microtitre plate. After the agar had solidified, the plate was seeded with bentgrass, *Agrostis palustris* Huds. (10–15 seeds per well), and covered with a lid. The plate was placed in a transparent plastic box lined with wet paper towels and the whole system was transferred to a growth chamber (Controlled Environments Inc., Pembina, ND, USA) set under continuous light (250 μmol m^{-2} h^{-1}) at 22 °C. The herbicidal activity of each well was visually assessed as percentage injury 7 days after planting, with 0 representing no injury and 100 representing no growth. The experiment was conducted three times.

2.6 Greenhouse study

The pre-emergence activity of metolachlor and *S*-metolachlor was determined on five different soils (Table 1). Flats (10 cm × 10 cm × 5 cm) were filled with each of the soils, and barnyardgrass, *Echinochloa crus-galli* L., seeds were planted 1 cm deep in a row in each flat. The flats were sprayed with a range of rates, depending on soil type (Table 2), of either metolachlor or *S*-metolachlor with an air-pressurised, moving head sprayer set to deliver 187 litre ha^{-1} at 280 kPa and 2.7 km h^{-1}. The flats were watered immediately after application with approximately 1 cm of water to incorporate the herbicides. Flats were placed in a greenhouse with natural light supplemented by halogen lamps to obtain a 14 h photoperiod with 27/14 °C day/night temperatures. The experiment was set up in a randomised complete block design with four replicates per treatment. The flats were watered as needed and fertilised once a week. After 3 weeks, plants were harvested and dried at 60 °C for 3 days, and dry weights were determined on a per plant basis. All experiments were repeated three times. The dry weight of the untreated plants across the soils ranged from 7 to 12 mg per plant.

2.7 Field study

The pre-emergence activity of metolachlor and *S*-metolachlor was evaluated at three field locations in eastern Colorado (Fort Collins, Berthoud and Yuma). All the fields were under conventional tillage and were planted with corn at 79 000 seeds ha^{-1} in rows 76.2 cm apart prior to herbicide application. The varieties planted were Golden Harvest 8250 (Golden Harvest Seeds Inc., Waterloo, NE, USA), DeKalb RR 44–46 (Monsanto Company, St Louis, MO, USA) and DeKalb DKC 60-19 (Monsanto Company) at Berthoud, Fort Collins and Yuma respectively. Soil characteristics of each site are

Table 2. Rate structure for pre-emergence test

Rate (kg ha^{-1})		
San Luis Valley	Gilcrest	Minnesota, Nebraska, Wisconsin
	0.026	
	0.035	0.035
0.052	0.052	0.052
0.070	0.070	0.070
0.105	0.105	0.105
0.140	0.140	0.140
0.210		0.210
0.280		0.280
		0.420

Table 3. Soil properties for field studies

Location	Soil series	pH	OM (%)
Berthoud, CO	Nunn clay loam	7.3	3.8
Fort Collins, CO	Fort Collins clay loam	7.8	2.1
Yuma, CO	Haxtun sandy loam	6.5	1.4

shown in Table 3. The sites were planted in corn and treated on 8, 13 and 18 May 2003 in Yuma, Fort Collins and Berthoud respectively. Metolachlor 934.6 g litre^{-1} EC and *S*-metolachlor 915.5 g litre^{-1} EC (Dual II® and Dual II MAGNUM® respectively, Syngenta Crop Protection) were applied at rates of 1.1, 0.83, 0.56 and 0.42 kg AI ha^{-1} in 168 litre ha^{-1} with a carbon dioxide-pressurised backpack sprayer. The plots were 3.1 m × 10 m and were in a randomised complete block design with three replications. All sites had a natural infestation of *E. crus-galli* and green foxtail, *Setaria viridis* L. The plots were treated with 0.42 kg AE ha^{-1} of dicamba 4 weeks after planting to control broadleaf weeds. The activity of the herbicides against *E. crus-galli* and *S. viridis* was evaluated as visual control at 8 weeks after application, with 0 representing no activity and 100 representing complete control compared with untreated plots.

2.8 Statistical analysis

Regression analysis was used to determine the effect of herbicide and herbicide dose on *E. crus-galli* on each soil type. *Echinochloa crus-galli* dose–response residual mean square and predicted sum of squares were examined and a form of the nonlinear rectangular hyperbolic model was fitted to the data for each herbicide.[13] The nonlinear model was of the form

$$y = y_{\max}\{1 - [\text{rate}/(\text{GR}_{85} + \text{rate})]\} \qquad (2)$$

where $y_{\max}$ is the maximum dry weight and GR_{85} is the dose required to reduce the dry weight by 85% between the upper and lower limits.

Injury data from the agar bioassay were subjected to regression analysis and fitted to a log-logistic dose equation to estimate the concentration that caused 50% injury (LD_{50}) values.[14] Each plate had four replicates for each treatment, with two plates per time period. The experiment was repeated.

3 RESULTS AND DISCUSSION

3.1 Batch slurry equilibration and dissipation of herbicide in soil solution

The binding of metolachlor to soil is highly dependent upon organic matter.[15,16] Analysis of variance (ANOVA) showed no interaction between experiments, so data were pooled. The K_d values for both metolachlor and *S*-metolachlor varied among the five soils (Table 4), ranging from ~1.6 in the sandy loams to ~6.9 in the Webster clay loam soil. There were no differences in K_d values between metolachlor and *S*-metolachlor. The extent of soil binding was highly correlated with the soil organic matter ($R^2 = 0.98$). These results are similar to those found in other studies, which showed that metolachlor adsorption on soil was linear with respect to soil organic matter and clay content.[15,16]

Table 4. Soil–herbicide partition coefficients (K_d) for metolachlor and *S*-metolachlor in five different soils, as determined by batch slurry equilibrium

	K_d (±SD) (ml g^{-1})	
Soil	Metolachlor	*S*-Metolachlor
Gilcrest	2.04 (±0.19)	1.98 (±0.18)
Minnesota	7.01 (±0.37)	6.93 (±0.33)
Nebraska	4.45 (±0.15)	4.27 (±0.25)
San Luis Valley	1.67 (±0.24)	1.58 (±0.13)
Wisconsin	3.58 (±0.26)	3.63 (±0.41)

Table 5. Dissipation of metolachlor and *S*-metolachlor in soil solution of five different soils[a]

	DT_{50} (days)	
Soil	Metolachlor	*S*-Metolachlor
Gillcrest	31	28
Minnesota	24	26
Nebraska	13	13
San Luis Valley	12	19
Wisconsin	14	19

[a] The time for 50% of the herbicide to dissipate (DT_{50}) was calculated by regression analysis. There were no statistical differences between the herbicides ($P = 0.05$).

The concentration of metolachlor and *S*-metolachlor in the soil solution reflected the binding of these herbicides to the soil. There was a much higher concentration of both chemicals in the soil solution in the sandy loams than in the Webster clay loam soil, with the Hastings and Plano clay loams being intermediate (Fig. 2). The concentrations of both herbicides in the soil solution decreased with time after treatment. The calculated rate of dissipation of metolachlor and *S*-metolachlor in the soil solution varied with soil type (Table 5), but there were no differences between metolachlor and *S*-metolachlor in a given soil. The half-lives for metolachlor in these five soils agree closely with values reported by others.[5] Metolachlor and *S*-metolachlor dissipation was probably due to a combination of microbial degradation and time-dependent binding of the herbicide to the soil, which has been reported by others.[17,18] However, since these soils had been air dried, microbial degradation could have been suppressed.

3.2 Microtitre plate bioassay

The activity of *S*-metolachlor on *A. palustris* in agar was greater than that of metolachlor on a gram for gram basis (Fig. 3A), with the LD_{50} for *S*-metolachlor being approximately 1.7-fold lower than that for metolachlor. *S*-Metolachlor is ~88% *S*

Pest Manag Sci **62**:617–623 (2006)
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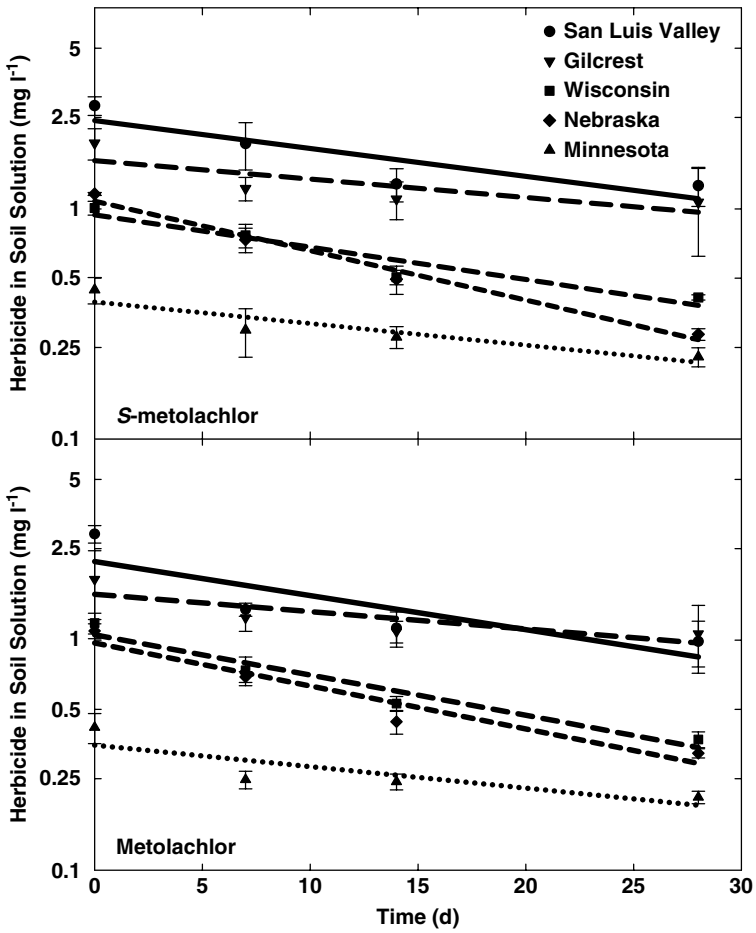

Figure 2. Dissipation of metolachlor and *S*-metolachlor in soil solution of five different soils. Fitted lines are linear regressions.

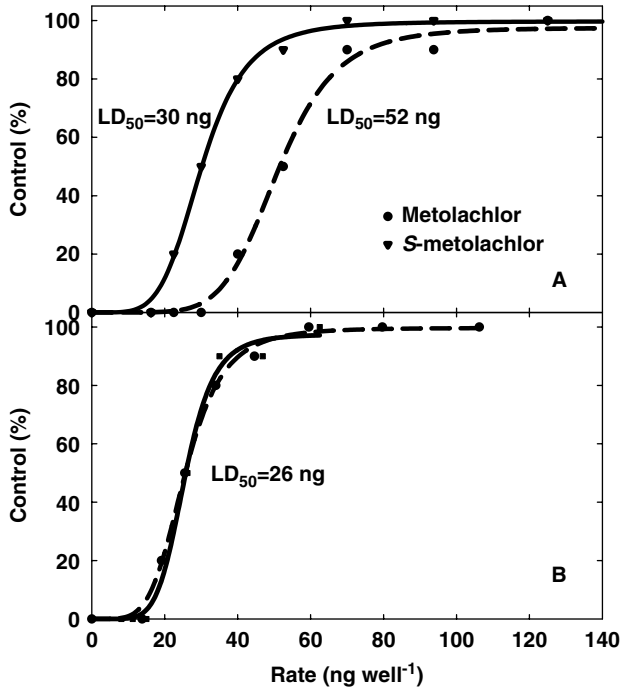

Figure 3. Herbicidal activity of metolachlor and *S*-metolachlor in agar on *Agrostis palustris*. Curves are log-logistic curves, with LD_{50} values calculated from the curves. (A) Comparison of metolachlor and *S*-metolachlor activity on a gram for gram basis. (B) Comparison of metolachlor and *S*-metolachlor activity corrected for *S*-metolachlor content of each herbicide (metolachlor, 50% *S*-metolachlor; *S*-metolachlor, 88% *S*-metolachlor).

isomer, while metolachlor is ~50% *S* isomer. When the bioassay results were adjusted for the concentration of *S*-metolachlor in each formulation, the inhibition curves coincided and the LD_{50} values were similar (Fig. 3B). These data indicate that the majority of the activity of metolachlor lies in the *S* isomers. The herbicidal activity of dimethenamid, another acetanilide, also resides in the *S* isomers.[4]

3.3 Greenhouse studies

Greenhouse studies showed that there were significant differences in activity between metolachlor and *S*-metolachlor in all five soil types against *E. crus-galli* (Table 6). The GR_{85} values were lower for the sandy loams than for the clay loam soils, and *S*-metolachlor was 1.4–3-fold more active than metolachlor across all soil types on a gram for gram basis. These data support previous work which showed that *S*-metolachlor is 1.4–1.6-fold more active than metolachlor on a gram for gram basis.[5] When the rates applied were corrected for the concentration of *S*-metolachlor in the formulation, there were no significant differences between the two herbicides, although the influence of soil type remained (Table 6).

3.4 Field studies

The results of the field studies supported the greenhouse observations. Statistical analysis showed

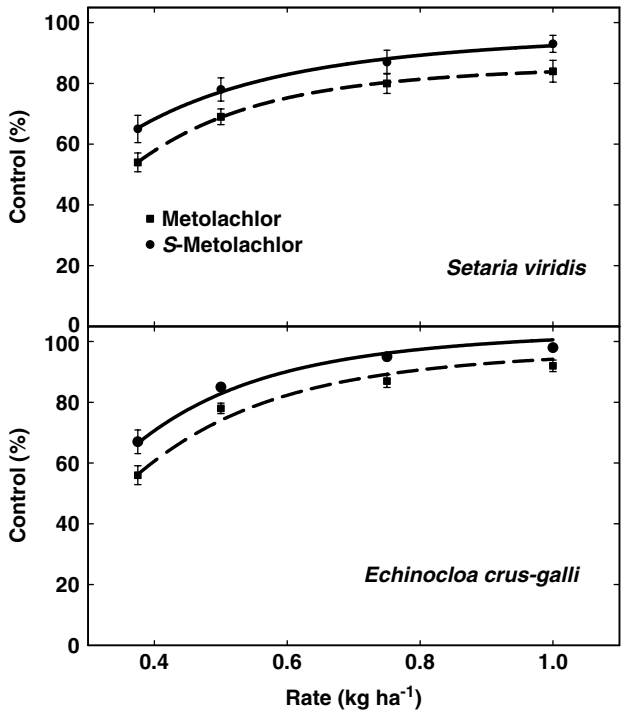

Figure 4. Herbicidal activity of metolachlor and *S*-metolachlor on *Setaria viridis* and *Echinochloa crus-galli* 8 weeks after treatment in three locations in Colorado.

no location interaction, so data were combined across sites. *S*-Metolachlor consistently gave significantly ($P = 0.05$) better control on a gram for gram basis than metolachlor of natural infestations of *E. crus-galli* and *S. viridis* (Fig. 4). When the rates for both herbicides were corrected for the concentration of the *S* isomer, the activities of the two herbicides were equivalent, which indicates that the contribution of the *R* isomer to the herbicidal activity is insignificant. These data are similar to those in previous studies which showed that most of the herbicidal activity of metolachlor is due to the *S* isomer.[3]

Table 6. Greenhouse activity of metolachlor and *S*-metolachlor on *Echinochloa crus-galli* in five soils

	GR_{85}[a] (g ha^{-1})			
	g g^{-1} basis		S-Met equivalent[b]	
Soil	Metolachlor	*S*-Metolachlor	Metolachlor	*S*-Metolachlor
Gilcrest	207a	59bc	104b	50c
San Luis Valley	92a	15b	46b	13b
Minnesota	241a	116b	122b	99b
Nebraska	125a	51b	63b	43b
Wisconsin	131a	43b	66b	37b

[a] Estimated concentration of herbicide that reduced dry weight by 85%.
[b] Adjusted GR_{85} values based on the concentration of *S*-metolachlor in each formulation.
Values followed by the same letter within each soil are not significantly different ($P = 0.05$).

4 CONCLUSIONS

These results show that most of the activity of metolachlor is due to the *S* isomer. There were no differences in soil binding or dissipation between metolachlor and *S*-metolachlor. If farmers use the generic form of metolachlor at the same rate, on a gram for gram basis, as *S*-metolachlor, then they will be applying less of the active isomer. The consequences of applying less of the *S* isomer to a field may or may not be immediately evident. The recommended metolachlor application rate varies with soil texture and organic matter. The Dual II MAGNUM® label recommends ~1 kg ha^{-1} on a coarse soil with an additional 0.1 kg ha^{-1} for each 1% of organic matter, whereas on a fine soil the recommendation is ~1.4 kg ha^{-1} with an additional 0.1 kg ha^{-1} for each 1% of organic matter.[8] Assuming that a farmer follows the label and applies the same amount of metolachlor or *S*-metolachlor to a light soil with low organic

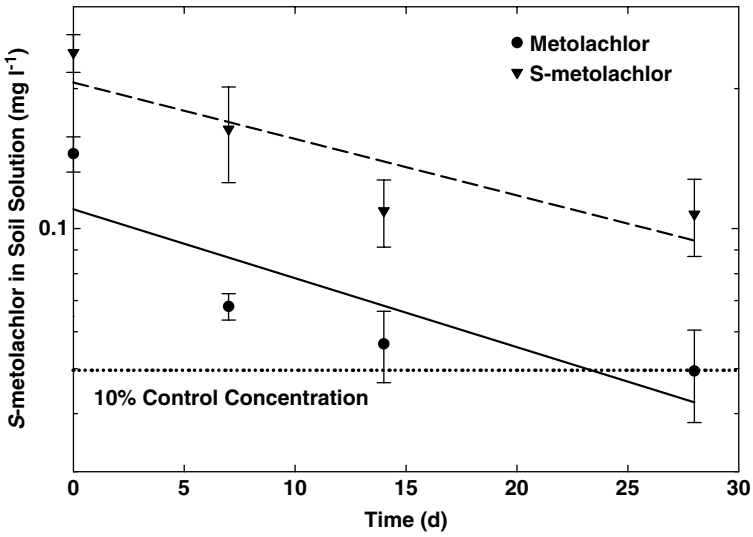

Figure 5. Hypothetical dissipation rate of metolachlor and *S*-metolachlor in San Luis Valley soil based on data shown in Fig. 3. Horizontal line indicates the concentration of *S*-metolachlor which did not control *Agrostis palustris* in agar bioassay.

Pest Manag Sci **62**:617–623 (2006)
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matter, the two herbicides may appear to be equally active under favourable conditions, i.e. as long as the concentration of *S*-metolachlor in the soil water is at or above that needed to control a particular weed. However, since the rate of dissipation of the herbicides is the same, the concentration of *S*-metolachlor in the soil solution will fall below the control threshold sooner with metolachlor than with *S*-metolachlor, and residual activity will be lower (Fig. 5). In addition, if a weed species present was on the edge of being controlled by *S*-metolachlor (a more difficult weed or weather condition), the weed may escape initial control by metolachlor as a result of the *S* isomer never reaching the control threshold for that weed or environment.

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